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SOLID AND LIQUID URANIUM

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REACTION OF WATER WITH
SOLID AND LIQUID URANIUM*

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Work in Progress

Introduction

In this study we observe the reaction of water $2\text{H}_2\text{O} + \text{U} \rightarrow \text{UO}_2 + \text{H}_2$ by measuring the evolution of H_2 as a function of the uranium temperature and of water pressure.

The equipment is a modulated molecular beam machine (viewgraph 2). A beam of H_2O molecules is formed by effusion from a quartz source tube, is periodically chopped by a synchronous chopper, and impinges on the target held horizontally in the target chamber (pressure $\sim 10^{-9}$ Torr). The reaction products are observed by a quadrupole mass spectrometer in the detection chamber (10^{-10} Torr).

Results

Viewgraph 3 shows the dependence of the reaction probability (H_2 formed per incident H_2O molecular) as a function of target temperature. (Solid circles and triangles.) The open symbols show the dependence of the signal phase on target temperature. (A reaction product signal that appears with a

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phase lag of 18° at a chopping frequency of 20 Hz indicates (to first order approximation) a reaction time at the uranium surface of $\frac{1}{20} \times \frac{18}{360} = \frac{1}{400}$ sec.)

Viewgraph 4 shows reaction probability (solid symbols) and phase (open symbols) as a function of chopping frequency. Viewgraph 5 depicts the dependency of reaction probability and phase on beam intensity.

Viewgraph 6 compares our measured reaction probability with the measurements of Carlos Colmenares, (60 Torr, 373 K). To make the comparison we deduce from Colmenares' data the reaction probability

$$\left(\frac{\text{nr. of O atoms incorporated}}{\text{nr. of H}_2\text{O molecules impinging}} \right)$$

at $p_0 = 60$ Torr and multiply by

$$\left(\frac{p (= 10^{-4} \text{ Torr})}{p_0 (= 60 \text{ Torr})} \right)^{\frac{1}{2.1} - 1}$$

Colmenares' data point fits well with an extrapolation of our data, and his activation energy is consistent with our data.

Reaction Models

Viewgraph 7 lists the steps that lead from the adsorption of H_2O to the formation of H_2 . (O is not balanced! η is the sticking coefficient.) If one assumes that all steps except one (i.e., the recombination of H on the surface, k_2) are fast, one is led to the results of viewgraph 8. It is apparent that the reaction is second order (in contrast to Colmenares', who found a weight gain proportional to $p^{\frac{1}{2.1}}$). This very simple reaction model fits the dependence of reaction probability and phase on pressure and chopping frequency at a fixed temperature very well (solid line, fig. 4, 5), but it

cannot fit the temperature dependence of the measured reaction probability which varies by a factor 50 (fig. 3), while the predicted ϵ varies only by $\cos\phi$ (last equation). Since the maximum measured ϕ is only $\sim 20^\circ$, this model is clearly insufficient.

In figures 9 & 10 we show a reaction model with two rate constants, k_i and k_s . There k_i controls the formation of UO_2 at the interface from OH and k_s controls the regeneration of O at the surface from an adsorbed OH.

Again we assume that the diffusion of OH and H is fast compared to the reaction steps. The model postulates a number "N" of sites at which the dissociation of H_2O and the instantaneous incorporation of OH occurs. It assumes that the sticking probability is reduced if these sites are occupied by surface-OH (concentration m). The model has six adjustable parameters (see viewgraph 11, bottom) which are chosen by an optimization routine such that there is minimum deviation between data and model over all parameter space. The dashed lines in all viewgraphs represent this 6 parameter model. Even though the adjustable parameters are physically reasonable and lead to a good fit, the model is clearly wrong, as shown in Fig. 11. Fig. 11 lists n_0 and m_0 , the average concentration (per cm^2) of OH at the surface (m_0) and at the interface (n_0). At all temperatures, pressures (intensities) and frequencies the OH concentration at the surface, m_0 , is a small fraction of a monolayer, whereas the OH concentration at the interface, n_0 , is always at least two orders of magnitudes higher. That is inconsistent with the model, which assumes OH diffusion from the surface to the interface, and does not incorporate any driving force that would justify diffusion against a concentration gradient. In addition the OH concentration at the interface, m_0 , is at the lowest temperature (373 K) equivalent to approximately 100 monolayers, again inconsistent with the model.

Summary

The reaction probability of water with solid and liquid uranium has been measured. The measurements are consistent with the data of Colmenares, extrapolated over 5 orders of magnitude in pressure (from 60 Torr to 10^{-4} Torr) and to higher temperatures using his activation energy and pressure dependence. The reaction probability is approximately 6×10^{-2} and constant above 800 K. There is certainly no dramatic change, maybe a small decrease, in the reaction probability as uranium melts.

Two simple surface reaction models have been tried and found to be unsatisfactory.



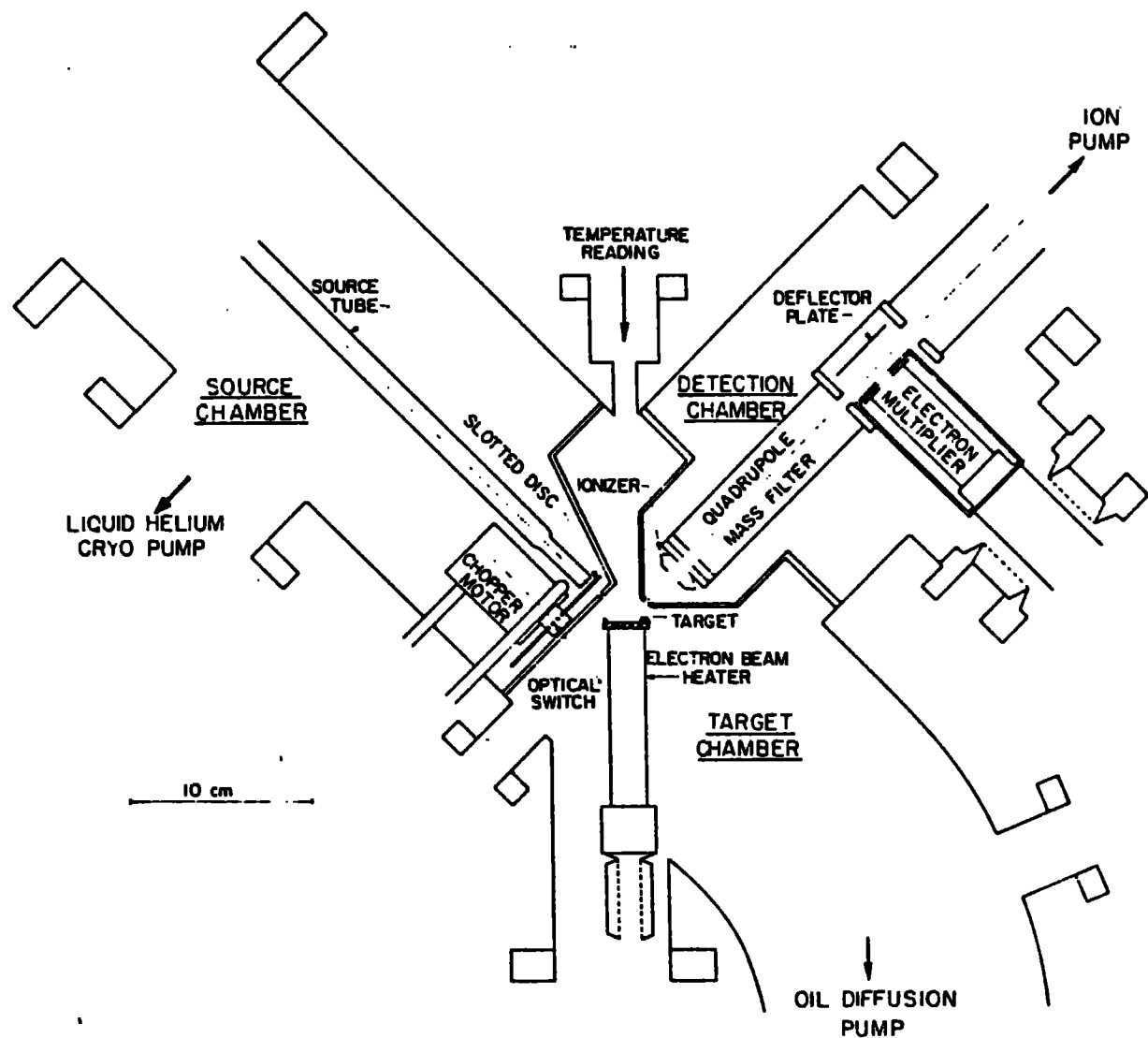
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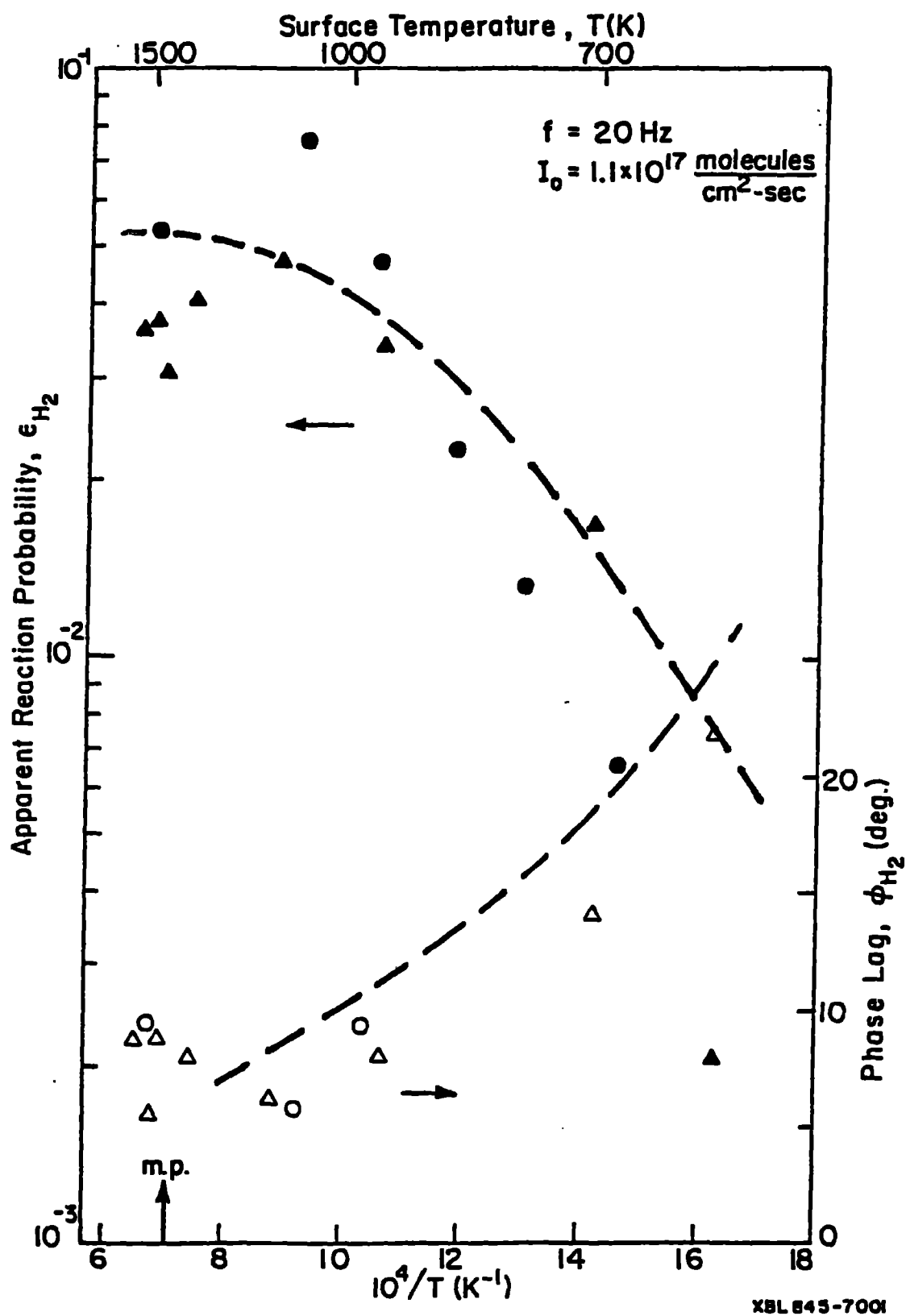


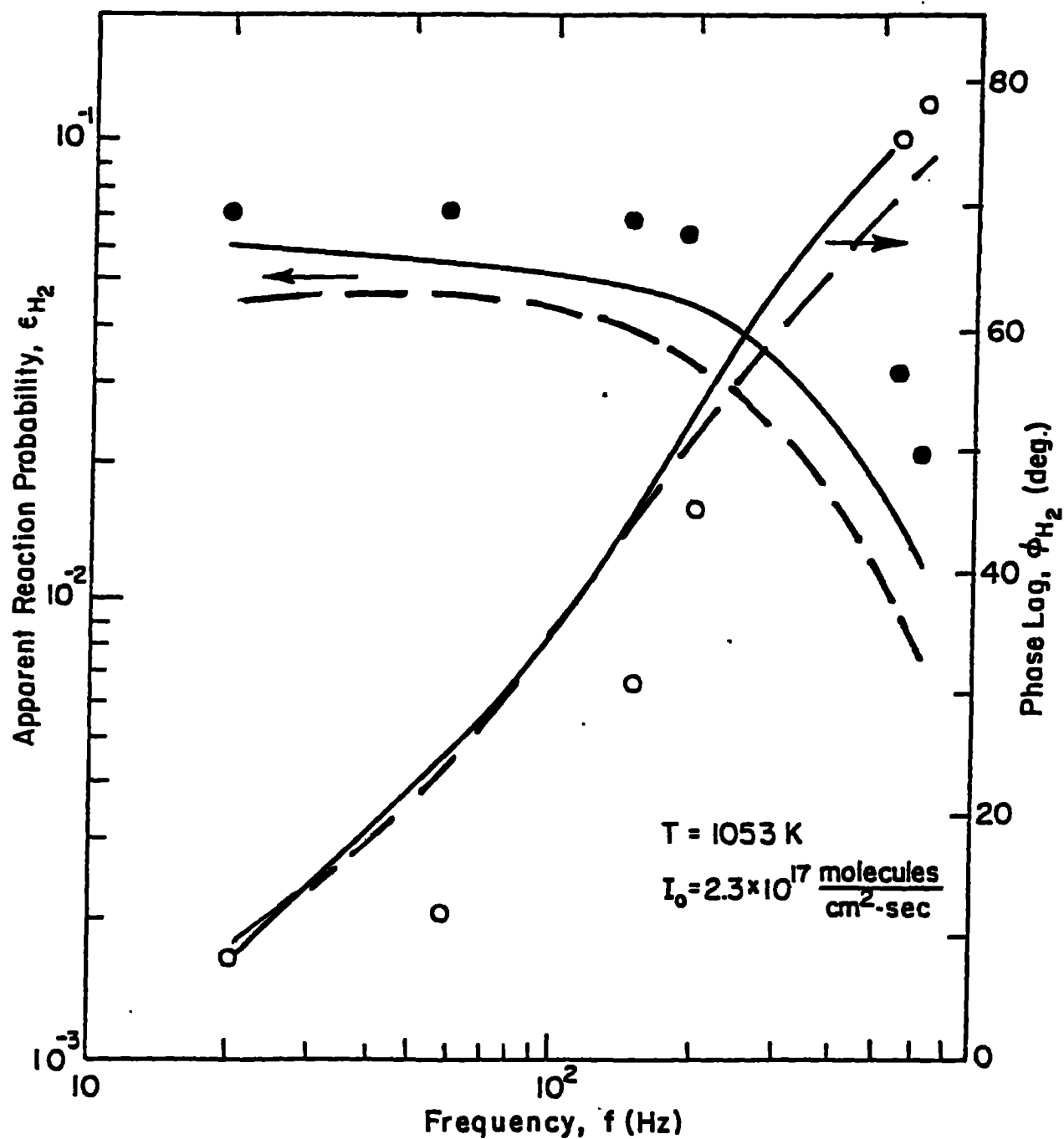
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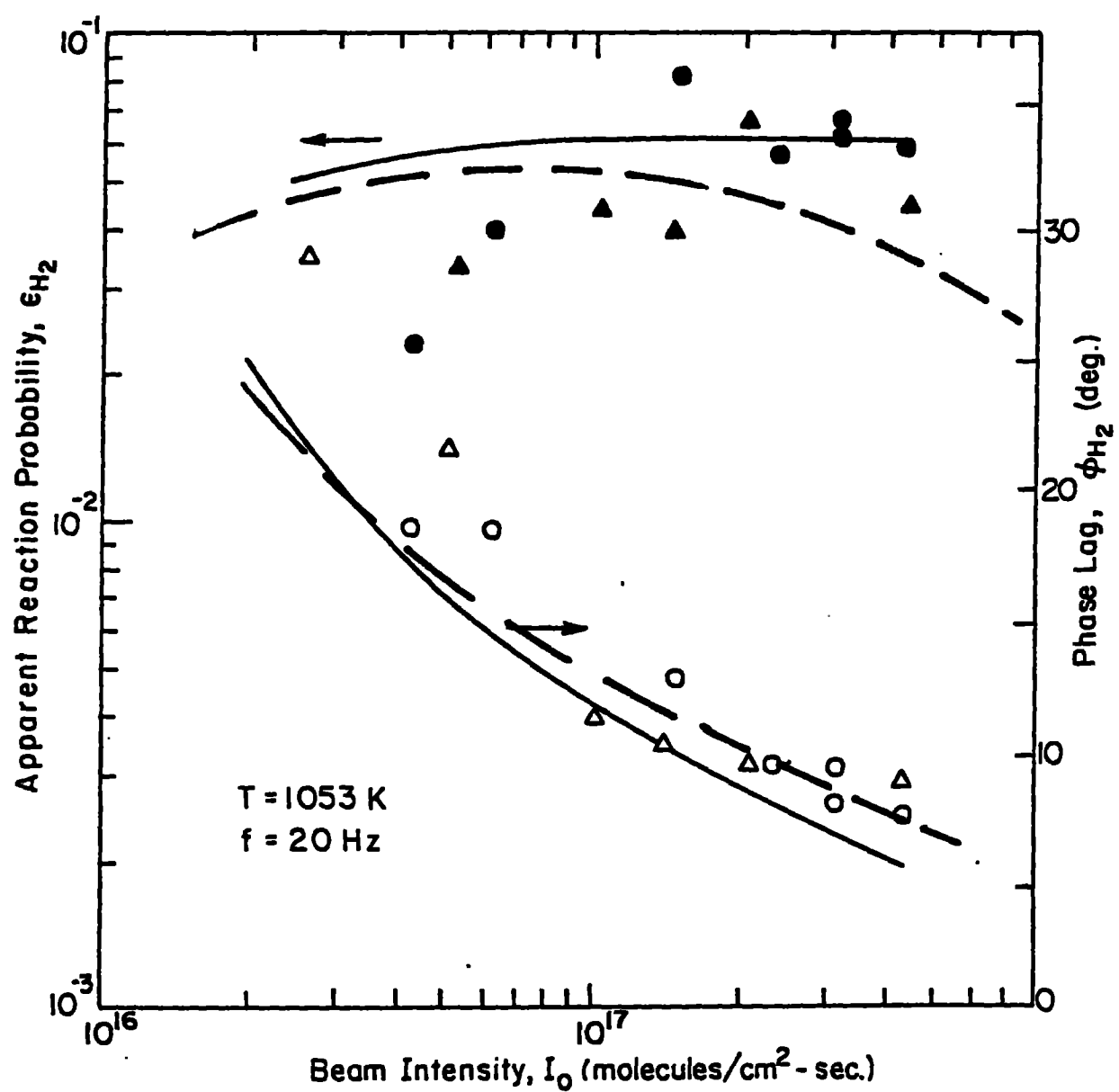
Fig. 2





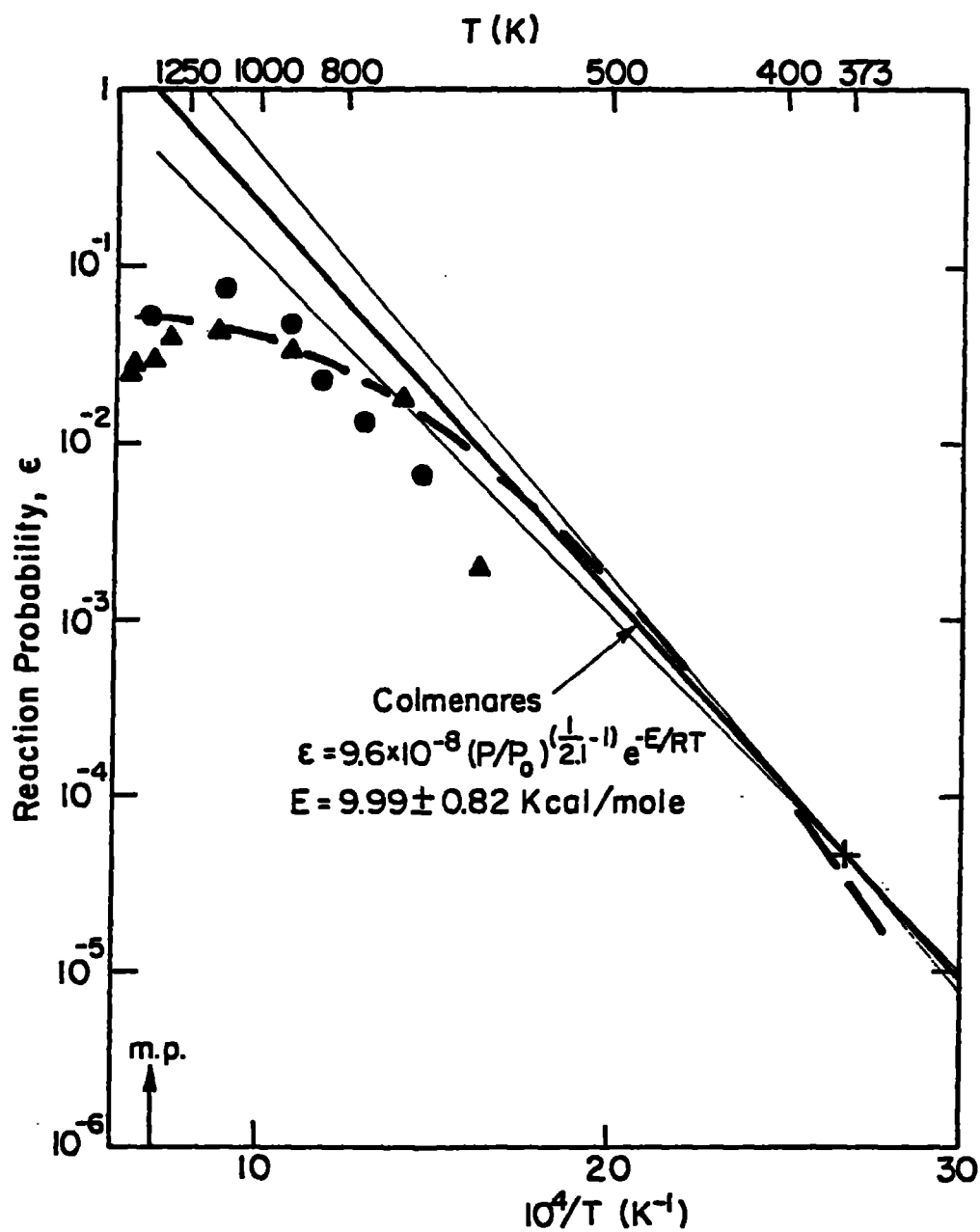
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Fig. 4



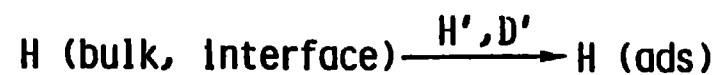
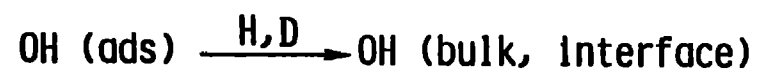
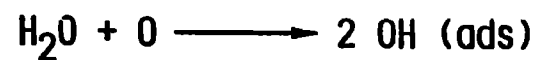
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Fig. 5



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Fig. 6



Assume $\text{D,H, D}',\text{H}', k_1}$ fast

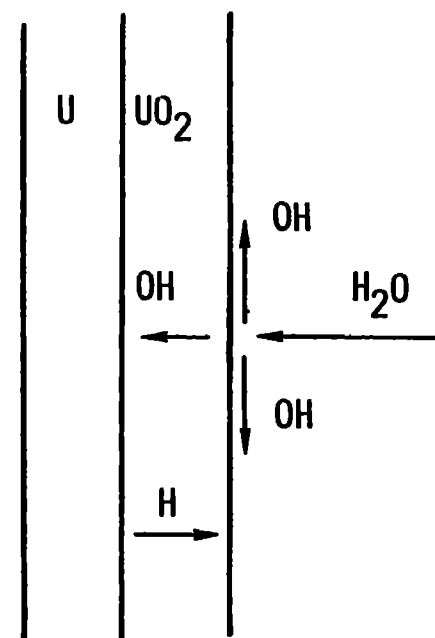


Fig. 7



Mass balance on H (ads)

n = concentration of H (ads)

$$\frac{dn}{dt} = 2 \eta I_0 g(t) - 2 k_2 n^2$$

$$n = n_0 + \tilde{n} e^{i\omega t}$$

$$n_0 = \sqrt{\frac{\eta I_0}{2 k_2}}$$

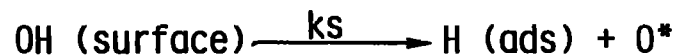
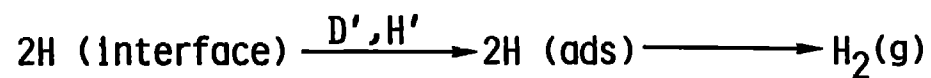
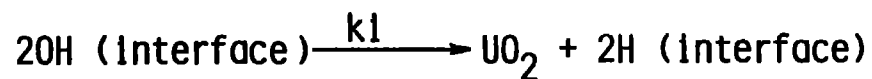
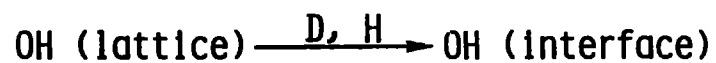
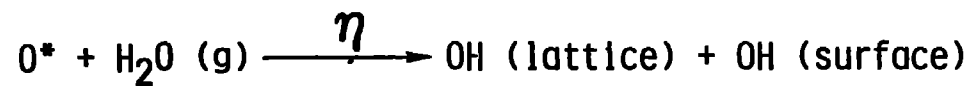
$$\tilde{n} = \frac{\eta I_0 g_1}{i\omega + \sqrt{8 k_2 \eta I_0}}$$

$$\epsilon e^{i\phi} = \frac{\eta}{1 + \frac{i\omega}{\sqrt{8 k_2 \eta I_0}}}$$

$$\tan \phi = \frac{\eta}{\sqrt{8 k_2 \eta I_0}}$$

$$\epsilon = \eta \cos \phi$$

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Assume D', H', D, H ; conc of H (ads) small
 m = conc. of OH at the surface
 n = conc. of OH at the interface
 o^* = conc. of O (lattice) at zero pressure
 $= \text{const.} = N$

Mass balance on OH

$$\frac{dm}{dt} = I_0 g(t) \left(1 - \frac{m}{N}\right) \eta - k_s m$$

$$\frac{dn}{dt} = I_0 g(t) \left(1 - \frac{m}{N}\right) \eta - 2 k_1 n^2$$

$$\epsilon e^{-\phi} = \frac{k_1 \tilde{n}^2 - \frac{1}{2} k_s \tilde{m}}{\frac{1}{2} I_0 g_1}$$



| FREQUENCY | INTENSITY | TEMP | NO | MO | QO |
|------------|------------|------------|------------|------------|----|
| .10000E+01 | .10000E+01 | .37300E+03 | .54936E+18 | .28720E+14 | 0. |
| .10000E+01 | .10000E+01 | .61300E+03 | .17110E+16 | .12735E+14 | 0. |
| .10000E+01 | .10000E+01 | .61300E+03 | .17110E+16 | .12735E+14 | 0. |
| .10000E+01 | .10000E+01 | .61300E+03 | .17110E+16 | .12735E+14 | 0. |
| .10000E+01 | .10000E+01 | .70300E+03 | .47110E+15 | .81639E+13 | 0. |
| .10000E+01 | .10000E+01 | .94300E+03 | .45606E+14 | .30974E+13 | 0. |
| .10000E+01 | .10000E+01 | .11330E+04 | .14083E+14 | .18192E+13 | 0. |
| .10000E+01 | .10000E+01 | .13430E+04 | .56191E+13 | .11872E+13 | 0. |
| .10000E+01 | .21000E+01 | .10600E+04 | .29381E+14 | .42535E+13 | 0. |
| .49000E+01 | .21000E+01 | .10600E+04 | .29381E+14 | .42535E+13 | 0. |
| .24900E+02 | .21000E+01 | .10600E+04 | .29381E+14 | .42535E+13 | 0. |
| .10000E+01 | .39000E+01 | .10600E+04 | .37808E+14 | .70434E+13 | 0. |
| .10000E+01 | .40000E+00 | .10600E+04 | .13629E+14 | .91524E+12 | 0. |
| .10000E+01 | .23000E+00 | .10600E+04 | .10402E+14 | .53318E+12 | 0. |

| AMP-DATA | AMP-THEORY | PHI-DATA | PHI-THEORY |
|------------|------------|------------|------------|
| .90000E-04 | .36877E-04 | .88000E+02 | .47547E+02 |
| .21000E-02 | .90786E-02 | .21800E+02 | .26841E+02 |
| .21000E-02 | .90786E-02 | .21800E+02 | .26841E+02 |
| .21000E-02 | .90786E-02 | .21800E+02 | .26841E+02 |
| .17000E-01 | .15844E-01 | .14000E+02 | .21539E+02 |
| .34000E-01 | .39291E-01 | .81300E+01 | .21992E+02 |
| .48000E-01 | .51602E-01 | .63400E+01 | .97081E+01 |
| .41000E-01 | .55121E-01 | .81300E+01 | .44122E+01 |
| .60000E-01 | .42916E-01 | .60000E+01 | .10333E+02 |
| .49000E-01 | .31814E-01 | .42000E+02 | .32930E+02 |
| .20000E-01 | .13316E-01 | .74000E+02 | .66459E+02 |
| .49000E-01 | .34538E-01 | .60000E+01 | .80921E+01 |
| .23000E-01 | .49947E-01 | .20000E+02 | .17980E+02 |
| .80000E-03 | .48163E-01 | .28000E+02 | .20487E+02 |

$$N = 3 \times 10^{13}$$

$$K_S = 3 \times 10^4 \exp \left[- \frac{6.5}{RT} \right]$$

$$\eta = 6 \times 10^{-2}$$

$$K_I = 1.1 \times 10^{-6} \exp \left[- \frac{26.8}{RT} \right]$$